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(71) 出願人 595073018

ポーレン化学産業株式会社

千葉県東葛飾郡関宿町桐ヶ作536

(72) 発明者 荒井 安彦

千葉県東葛飾郡関宿町桐ヶ作536 ポーレン化学産業株式会社内

(72) 発明者 大西 明憲

三重県松阪市八太町828

(72) 発明者 小高 一夫

神奈川県横浜市鶴見区元宮1丁目10番21号

(72) 発明者 阿部 国弘

千葉県千葉市稲毛区小仲台2丁目13番9号

(74) 代理人 弁理士 長谷川 一 (外1名)

(54) 【発明の名称】 低発泡エチレン重合体樹脂積層帯電防止性シート

(57) 【要約】

【目的】 帯電防止性能を有し、かつ緩衝性及び良好な深絞り成形性を有する積層シートを提供する。

【構成】 発泡倍率が1.01~3倍であるエチレン重合体樹脂層(A層)及びオレフィン系重合体100重量部に対して帯電防止剤0.1~5重量部を含有するオレフィン系重合体組成物層(B層)からなることを特徴とする低発泡エチレン重合体樹脂積層帯電防止性シート。

## 【特許請求の範囲】

【請求項1】発泡倍率が1.01～3倍であるエチレン重合体樹脂層(A層)及びオレフィン系重合体100重量部に対して帯電防止剤0.1～5重量部を含有するオレフィン系重合体組成物層(B層)からなることを特徴とする低発泡エチレン重合体樹脂積層帯電防止性シート。

【請求項2】エチレン重合体樹脂が、メルトフローレート0.1～10g/10分、メルトテンション2～20gの物性を示すものである、請求項1に記載のシート。

【請求項3】エチレン重合体樹脂が、Q値2～9の物性を示すものである、請求項1に記載のシート。

【請求項4】エチレン重合体樹脂が、高圧法により製造された低密度エチレン単独重合体、エチレン・酢酸ビニル共重合体、及び、中低圧法により製造された高密度エチレン単独重合体、エチレンと他の $\alpha$ -オレフィンとの線状共重合体の中から選択された少なくとも一種である、請求項1に記載のシート。

【請求項5】発泡セルの平均寸法が0.05～0.5mmである、請求項1に記載のシート。

【請求項6】A層の厚みが0.1～5mm及びB層の厚みが20～2000 $\mu$ mである、請求項1に記載のシート。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、帯電防止性能を有し、かつ緩衝性及び良好な深絞り成形性を有する積層シートに関するものである。

## 【0002】

【従来の技術】熱可塑性樹脂シートを真空成形、圧空成形、真空・圧空成形、型押成形等の熱成形法によって製造される容器、内ケース(ゲス)、トレイ、下敷き等の各種成形体は、比較的安価であることから広く使用されている。しかしながら、これら成形体の中には、堅く、剛性が大き過ぎて使用できないとか、割れると怪我をし易いとか、触った時の感触をもっと改良したいと言った問題があった。

【0003】具体的には、物品の形状に合致する凹部を形成したシートの場合、例えば、IC収納ケースや金属缶収納用ケース等では堅すぎて収納する製品に傷を付け易いとか、アンプル、化粧品及び洋酒等のガラス製品収納用ケースでは滑り易いためにガラス製品等を落とし易いとか、人体に接するパット類では使用するに際し堅すぎるとか、玩具用お面等では割れた部分で顔や指を怪我をし易いとか、等々の問題があった。そのため、上記具体例の場合においては、ビロード布を積層した紙シートや、綿を入れた布製品としたり、或いは、高発泡の樹脂シート等が使用しているのが現状である。

【0004】しかし、紙では高級感を出しにくく、布製品では製造工程が繁雑になってコスト高となると言っ

た問題がある。また、高発泡の樹脂シートでは、例えば、発泡ポリスチレンの場合には、材質が堅すぎて変形した時の回復性に劣っており、初期の形状を保持することが難しかったり、シート熱成形に不向きであると言った問題があり、発泡ポリプロピレンの場合には、材質が堅すぎる以外に均一で良好な深絞りシート熱成形ができないと言った問題があり、発泡ポリウレタンの場合には鮮明な形状に賦形することができず、収納する製品をきちんと収めることができないと言った問題がある。

## 【0005】

【発明が解決しようとする課題】そこで、高発泡の樹脂シート材料として発泡ポリエチレンも考えられるが、単に発泡ポリエチレンを使用してシート熱成形をしても、熱成形を行なう際に、発泡セルが破れ易く、深絞り成形や絞り形状を鮮明に成形しようとして鋭角に成形すると、発泡体が局部的に強く引き伸ばされると発泡セルが破れるので事実上、絞り形状が鮮明な深絞り成形体や複雑な絞り形状の成形を行なうことができず、良好な成形体が得られないと言った問題がある。

【0006】また一方、容器、内ケース(ゲス)、トレイ、下敷き等の各種成形体に収納される製品によっては、例えば、電子部品や電気部品を備えた製品等は静電気を嫌うため特に注意を要する。そのため通常、帯電防止性包装材で包装するのが一般的であるが、外に緩衝材をも必要とする場合が一般的であるので煩雑で不経済でもあると言った問題がある。

【0007】従って、本発明は、帯電防止性能を有し、かつ緩衝性を有すると共に、発泡状態が良好に維持されたまま絞り形状が鮮明な深絞り成形を行なうことができる低発泡エチレン重合体樹脂積層シートを提供することを目的とするものである。

## 【0008】

【課題を解決するための手段】本発明者らは、上記問題点に鑑みて鋭意研究を重ねた結果、特定な性状の低発泡エチレン重合体樹脂層と帯電防止性オレフィン系重合体組成物層からなる積層シートにより、上記目的を達成することができるとの知見を得て、本発明を完成するに至ったものである。

【0009】すなわち、本発明は、発泡倍率が1.01～3倍であるエチレン重合体樹脂層(A層)及びオレフィン系重合体100重量部に対して帯電防止剤0.1～5重量部を含有するオレフィン系重合体組成物層(B層)からなることを特徴とする低発泡エチレン重合体樹脂積層帯電防止性シートである。

## 【0010】

## 【発明の実施の形態】

## 【I】原材料

## (1) エチレン重合体樹脂

## (a) 種類

本発明積層シートの上記A層を構成するエチレン重合体

樹脂としては、エチレンの単独重合体、或いは、エチレンを主要な構成成分とし、これと他の $\alpha$ -オレフィン及び/又は他の不飽和単量体との共重合体を挙げることができる。上記 $\alpha$ -オレフィンとしては、例えば、プロピレン、ブテン-1、3-メチルペンテン-1、4-メチルペンテン-1、ヘキセン-1、オクテン-1等の炭素数3~12程度、好ましくは3~8の $\alpha$ -オレフィンを挙げることができる。また、上記他の不飽和単量体としては、例えば、アクリル酸、メタクリル酸、アクリル酸メチル、メタクリル酸メチル、無水マレイン酸等の不飽和カルボン酸又はその誘導体；酢酸ビニル、酪酸ビニル等のビニルエステル；スチレン、メチルスチレン、ジビニルベンゼン等の不飽和芳香族単量体；ビニルトリメトキシシラン、 $\gamma$ -メタクリルオキシプロピルトリメトキシシラン等のビニルシラン等を挙げることができる。

【0011】これらの中でも、発泡成形性や真空成形性から好ましいエチレン重合体樹脂は、高圧法で製造される低密度エチレン単独重合体、エチレンを主成分とするエチレンと酢酸ビニル、アクリル酸、アクリレート、メタクリル酸、メタクリレート等との共重合体；中低圧法で製造される高密度エチレン単独重合体、エチレンを主成分とするエチレンと他の $\alpha$ -オレフィン（プロピレン、ブテン-1、ヘキセン-1、オクテン-1等）との線状共重合体等を挙げることができる。これら共重合体は、二元共重合体に限らず、三元以上の共重合体であっても良い。これらの中でも、特に好ましいエチレン重合体樹脂は、高圧法で製造される低密度エチレン単独重合体（LDPE）、エチレン・酢酸ビニル共重合体（EVA）、中低圧法で製造される高密度エチレン単独重合体（HDPE）、エチレンと他の $\alpha$ -オレフィンとの線状共重合体（L-LDPE）である。上記エチレン重合体樹脂中の $\alpha$ -オレフィン及び/又は他の不飽和単量体のエチレン重合体樹脂中での含有量は、本発明の効果を著しく損なわない限りエチレンが最多成分である範囲で構わないが、一般には30重量%以下、特に15重量%以下であることが好ましい。

#### 【0012】(b) 物性

上記エチレン重合体樹脂の物性は、MFR（メルトフローレート）が一般に0.1~10g/10分、更に好ましくは0.2~8g/10分、特に0.3~6g/10分、MT（メルトテンション）が一般に2~20g、更に好ましくは3~16g、特に好ましくは4~12gであることが好ましい。更に、エチレン重合体樹脂は、Q値（分子量分布）が一般に2~9、更に好ましくは3~8、特に好ましくは4~7であることが望ましい。上記MFRの値が低すぎると発泡体の表面光沢が悪くなる傾向があり、一方、高すぎると機械的強度が悪くなる傾向がある。また、MTの値が低すぎると高倍率の発泡体を得ることが難しくなる傾向があり、一方、高すぎると発泡セルが荒くなる傾向がある。Q値の値が低すぎると真

空成形性が低下する傾向があり、一方、高すぎると発泡体の衝撃強度が悪くなる傾向がある。

#### 【0013】(2) 発泡剤

該エチレン重合体樹脂を発泡させるのに用いる発泡剤としては、低発泡に使用されるものであれば種類を問わず使用できるが、例えば、アゾジカルボンアミド、重炭酸ソーダ・クエン酸、重炭酸ソーダ等の化学発泡剤であっても、ブタン、ペンタン、ヘキサン、ブタノール等の物理発泡剤であっても構わない。どちらかと言うと上記化学発泡剤を使用する方が低発泡に適量的气体量が発生することができる点で好ましい。これら発泡剤の中でもアゾジカルボンアミドを用いることが特に好ましい。また、これら発泡剤は併用して用いることもできる。

#### 【0014】(3) オレフィン系重合体

本発明積層シートの上記B層を構成するオレフィン系重合体としては、エチレン、プロピレン、ブテン-1、3-メチルペンテン-1、4-メチルペンテン-1、ヘキセン-1、オクテン-1等の炭素数2~12程度、好ましくは2~8の $\alpha$ -オレフィンの単独重合体、或いは、これら $\alpha$ -オレフィン同志の共重合体、更には、 $\alpha$ -オレフィンを主成分とする $\alpha$ -オレフィンと他の不飽和単量体との共重合体を挙げることができる。ここで、他の不飽和単量体としては、例えば、アクリル酸、メタクリル酸、アクリル酸メチル、メタクリル酸メチル、無水マレイン酸等の不飽和カルボン酸又はその誘導体；酢酸ビニル、酪酸ビニル等のビニルエステル；スチレン、メチルスチレン、ジビニルベンゼン等の不飽和芳香族単量体；ビニルトリメトキシシラン、 $\gamma$ -メタクリルオキシプロピルトリメトキシシラン等のビニルシラン；ブタジエン、イソブレン、エチリデンノルボルネン、ジシクロペンタジエン、1,4-ヘキサジエン等の共役又は非共役のジエン等を挙げることができる。また、共重合体の形態はランダム、ブロックまたはグラフト等を問わない。

【0015】該オレフィン系重合体は、樹脂状、ゴム状を問わないが、成形性、剛性等の点から樹脂状のものが好ましい。中でも好ましいものは、エチレン系重合体樹脂又はプロピレン系重合体樹脂である。ここで、エチレン系重合体樹脂としては上記のエチレン重合体樹脂を使用するのが望ましく、また、プロピレン系重合体樹脂としてはプロピレンの結晶性単独重合体、プロピレンを主成分とするプロピレンと他の $\alpha$ -オレフィン（エチレン、ブテン-1等）又はその他の不飽和単量体との二元又は三元以上の結晶性共重合体を挙げることができる。

#### 【0016】(4) 帯電防止剤

本発明積層シートの上記B層を構成するもう一方の成分である帯電防止剤としては、エチレングリコール、ジエチレングリコール、グリセリン、トリメチロールプロパン、ペンタエリスリット、ソルビット等の多価アルコールとラウリン酸、パルミチン酸、ステアリン酸等の飽和

脂肪酸又はオレイン酸、リノール酸等の不飽和脂肪酸との脂肪酸エステルや、ポリエチレングリコールを脂肪酸でエステル化した脂肪酸エステル或いは高級アルコールを有機酸又は該酸無水物と反応させて得られる高級アルコールのエステル等のエステル類；ラウリルアルコールやマッコウアルコール等の高級アルコールの硫酸エステルソーダ塩、ドデシルベンゼンスルホン酸ソーダ塩のような硫酸エステル塩類や硫酸スルホン酸塩類；高級アルコールと無水リン酸又はオキシ塩化リンなどとの反応により得られるリン酸エステル塩類；ポリオキシエチレンアルキルアミン等のアミン類；ポリアミド樹脂、ポリアミドアミン、アルキルジエタノールアミド等のアミド類；ラウリルトリメチルアンモニウムクロライドのような第4級アンモニウム塩；ペタイン類；アミノ酸類；エチレンオキサイド付加物等々の化合物を挙げることができる。中でも、グリセリン脂肪酸エステル、ポリグリセリン脂肪酸エステル、ポリオキシエチレンアルキルアミン、アルキルジエタノールアミド及びこれらの併用が好ましい。

#### 【0017】(5) その他任意成分

本発明の積層シートを構成するエチレン重合体樹脂及び／又はオレフィン系重合体中には、本発明の効果を著しく損なわない範囲で、上記必須成分以外にその他の任意成分を配合することができる。この任意成分としては、例えば、物性及び外観等の調整の目的で、エラストマー成分や他の樹脂成分、或いは、酸化防止剤、熱安定剤、光安定剤、着色剤、導電性付与剤、抗菌剤、防黴剤、防錆剤、気泡調整剤（発泡促進剤）、発泡剤分解温度調整剤、中和剤、分散剤、分子量調整剤（ラジカル発生剤等）、架橋剤、架橋助剤、造核剤、充填剤、滑剤、難燃剤、難燃助剤、加工助剤、重金属不活性化剤、可塑剤、蛍光増白剤、離型剤、軟化剤、光沢付与剤等の各種添加剤成分等を挙げることができる。

#### 【0018】(II) 積層シートの製造

本発明の積層シートを製造するには、種々の方法を採用することができるが、一般には、先ず上記エチレン重合体樹脂に、発泡剤及び場合により他の任意成分を配合し、これを熔融混練して押出して低発泡エチレン重合体樹脂シート（低発泡シート：A層となる）を製造する。別に、上記オレフィン系重合体に帯電防止剤及び場合により他の任意成分を配合し、これを熔融混練して押出してオレフィン系重合体組成物シート又はフィルム（帯電防止シート又はフィルム：B層となる）を製造する。これら低発泡シートと帯電防止シート又はフィルムの両者を適当な接着剤を使用し、又は接着剤を使用せずに熱融着で積層する。このとき、これらシート又はフィルムの両方又は片方が溶融状態であっても良く、共押出法で積層することもできる。

【0019】(1) 低発泡エチレン重合体樹脂シートの製造

エチレン重合体樹脂に、発泡剤を一般に0.01~0.2重量%、好ましくは0.02~0.1重量%、特に好ましくは0.02~0.07重量%の割合で配合し、これらを通常の混練押出機、例えば、一軸押出機、二軸押出機等で、樹脂温度が一般に170~240℃、好ましくは180~230℃の温度条件下で熔融混練し、ダイのスリットより押し出すことにより、発泡倍率1.01~3倍、好ましくは1.1~2倍、特に好ましくは1.3~1.8倍に発泡させて、厚さが一般に0.1~5mm、好ましくは0.2~3mmの低発泡エチレン重合体樹脂シート（低発泡シート）を製造することができる。このシートは非架橋の低発泡シートとして得られる。

【0020】上記発泡倍率が低すぎると柔軟性に劣ったものができると共に、次の熱成形工程において美麗な賦形ができないときがある。一方、発泡倍率が高すぎると、次の熱成形工程において成形が不良となる。ここで得られる低発泡シートは、後記熱成形時においても、発泡状態が良好に維持されたまま、引きつることなく成形することができるので、絞り形状を鮮明に成形することができ好ましい。

【0021】上記成形によって、低発泡シート中に多数の発泡セルが生じるが、本発明で使用する低発泡シートにおいては該発泡セルが微細で、それらが均一で、該発泡セルの平均寸法が、一般に0.05~0.5mm、好ましくは0.1~0.4mm、特に好ましくは0.15~0.3mmの範囲にあるものが、後記熱成形された際にも発泡セルが破壊され難く、発泡状態が良好に維持されたまま絞り形状を鮮明に出せるので好ましい。この様な発泡セルの平均寸法は、発泡剤の種類、その量、その配合時の条件を適宜選択することによって調製することができる。

#### 【0022】(2) オレフィン系重合体組成物シート又はフィルムの製造

オレフィン系重合体に、その100重量部に対して一般に0.1~5重量部、好ましくは0.3~4重量部、特に好ましくは0.3~3重量部の帯電防止剤を配合し、これらを通常の混練押出機、例えば、一軸押出機、二軸押出機等で熔融混練し、ダイのスリットより押し出すことにより、厚さが一般に20~2000μm、好ましくは30~1500μmの帯電防止性のオレフィン系重合体組成物シート又はフィルム（帯電防止シート又はフィルム）を好適に製造することができる。上記帯電防止剤が少な過ぎると満足な帯電防止性が得られずに静電気防止機能を付与することができず、一方、多過ぎると成形性が悪化して成形外観が悪くなる外に耐衝撃性も低下するので好ましくない。

#### 【0023】(3) 積層

上記低発泡シートと帯電防止シート又はフィルムとを積層するには、適当な接着剤、例えば、溶剤型の二液硬化型ウレタン系接着剤、ウレタンエマルジョン系水性接着

剤等を介してロール等で圧着して積層する、いわゆるドライラミネート法に依っても良く、また、低発泡シートと帯電防止シート又はフィルムとを接着剤を用いずに熱圧着して溶融一体化して積層しても良い。更には、低発泡シートと帯電防止シート又はフィルムとの両方、又は片方を溶融状態で会合させて積層する、いわゆる共押出法に依って積層しても良い。特に、共押出法では厚みの調節がし易く経済的でもあるので好ましい。なお、本願発明における積層シートは、これら2層からなることを特徴とするものであることから、これら2層を構成している限り3層であっても、また他の基材との積層であっても構わなく、例えば、低発泡シートの両面に帯電防止シート又はフィルムを積層したものであっても、また布や樹脂フィルム等を更に積層したものであっても良い。

#### 【0024】III 熱成形

上記低発泡シート層(A層)と帯電防止シート又はフィルム層(B層)との積層体は、好適には以下に示す真空成形法、圧空成形法、真空・圧空成形法、型押成形法等の各種熱成形法により、加熱されて軟化した状態で、これに真空又は加圧等の手段により外力を加えて変形させ、各種形状に賦形させた後、冷却することによって種々の目的のシート熱成形体が得られる。

##### 【0025】(1) 真空成形法

上記真空成形法としては、雌型或いは雄型のいずれか一方のみを使用して、積層シートを加熱軟化させた後、型の上に載せ、該シートと型との間隙を真空にして積層シートを型の表面に密着させ、冷却して成形する方法である。具体的には、ストレート成形、ドレープ成形、プラグアシスト成形、プラグアシスト・リバースドロー成形、エアスリップ成形、スナップバック成形、リバースドロー成形、プラグアシスト・エアスリップ成形、フリー成形、マッチモールド成形、プラグリング成形、スリップ成形、接触加熱成形等の公知の各種の成形方法を採用することができる。

##### 【0026】(2) 圧空成形法

上記圧空成形としては、上記真空成形が大気圧を利用するのに代わり、圧縮空気で加熱軟化させた積層シートを型に圧着して成形する方法である。

##### (3) 真空・圧空成形法

上記真空・圧空成形法としては、上記真空成形と圧空成形とを組み合わせて成形する方法である。

##### (4) 型押成形法

上記型押成形法としては、加熱軟化させた積層シートを上下の台盤の間に挿入して型で押して成形する方法、或いは、積層シートをそのまま加熱された型で押圧させて成形する方法である。

上記熱成形は、通常の熱成形装置により常法に従って行なわれる。

#### 【0027】深絞り

一般にシートの熱成形では、良好な発泡状態を維持した

まま絞り形状が鮮明に出るように、通常30mm以上の深さにまで絞る深絞り成形を行なうことは難しいが、本発明の積層シートにおいては、意外にも30mm以上、好ましくは40mm以上、特に好ましくは50mm以上、の深さにまで深絞り成形することができる。該深絞り成形は、該シート面と深絞りされた壁面とを、ほぼ直角程度の角度、極端には逆テーバーにまで折り曲げて成形することができることから、絞り形状を鮮明に成形することができる。この時、高度な深絞り成形を行なうことができるのは、発泡セルが微細で、その寸法が均一であるために、熱成形した際にも発泡セルが破れず、良好な発泡状態が維持されたまま、一方向に偏ることなく均等に深絞り成形ができるからであるものと推定している。本発明の様に、上記積層シートを熱成形材料として使用することにより、上記の様な深絞り成形が達成されたことは意外なことであった。なお、本発明は、熱成形において絞らない成形体にも応用できることは勿論である。

#### 【0028】(5) 裁断

上記各種形状に熱成形された熱成形体を、各種用途に合致する様に裁断して、熱成形機上の積層シートより切り離すが、一般的には、裁断刃にて打ち抜く方法により行なわれる。この時、前記エチレン重合体樹脂原料中に、予め、通常ポリオレフィンのブロッキング防止剤として使用されているものを微量添加しておく、と、裁断時の刃離れが良く、打ち抜き性が良好となるので好ましい。

#### 【0029】IV 積層シート熱成形体の用途

この様な本発明の積層シートからなる熱成形体においては、大きな深さの深絞り成形を施すことができることから、各種用途に適用される種々の熱成形体に成形することができる。該熱成形体の用途としては、例えば、IC、プリント配線基板、電子部品、精密機械部品、塵埃を嫌う各種製品等の帯電防止性収納ケースを挙げることができる。

#### 【0030】

【実施例】以下に示す実験例によって、本発明を更に具体的に説明する。

##### I 原材料

##### (1) A層を構成するエチレン重合体

LDPE(高圧低密度エチレン単独重合体): MFR 4 g/10分、MT 5 g、Q値 6. 2

LDPE(高圧低密度エチレン単独重合体): MFR 0. 3 g/10分、MT 12 g、Q値 6. 0

EVA(エチレン・酢酸ビニル共重合体): MFR 0. 5 g/10分、MT 11 g、Q値 5. 5

HDPE(高密度エチレン単独重合体): MFR 0. 6 g/10分、MT 9 g、Q値 5. 6

L-LDPE(エチレンと7重量%のブテン-1との共重合体): MFR 0. 8 g/10分、MT 5 g、Q値 7. 0

## 【0031】(2) 発泡剤

AA : アゾジカルボンアミド

CS : 重炭酸ソーダ・クエン酸の1:1混合系

## 【0032】(3) B層を構成するオレフィン系重合体

HDPE (高密度エチレン単独重合体) : MFR 0.6 g/10分

EPP (プロピレン・エチレンブロック共重合体) : MFR 33 g/10分 (230℃、2.16 kgf 荷重) : 23℃キシレン可溶分12重量% : 上記可溶分中のプロピレン含量60重量%

## (4) 帯電防止剤

グリセリン脂肪酸エステル : 花王(株)製、商品名「エレクトロストリッパー TS-5」

ポリグリセリン脂肪酸エステル : ライオン(株)製、商品名「アーモスタット DGS」

N, N-ビス(2-ヒドロキシエチル)脂肪酸アミン : ライオン(株)製、商品名「アーモスタット 310」

## 【0033】(II) 評価方法

## (1) 樹脂物性

MFR

メルトフローレート(MFR)は、JIS K7210の規定により、温度190℃、荷重2.16 kgf によって測定した値である。

M T

メルトテンション(MT)は、東洋精機(株)製キャビロクラフを用い、溶融降下スピード10 mm/分、温度190℃で押し出し、引取スピード4 m/分によって測定した値である。

Q 値

Q値(分子量分布)は、ゲルパーミエーションクロマトグラフィー(GPC)によって測定した値である。

## 【0034】(2) 評価

発泡倍率

発泡倍率は、ピクノメーターを用いて発泡前と発泡後の密度を測定し、発泡前の密度を発泡後の密度で除した値である。

発泡セル寸法

発泡セルの平均寸法は、発泡体の厚さ方向及び平行方向にスライスした面を顕微鏡を用いて拡大透視し、気泡の

平均寸法を測定した値である。

絞り深さ

成形体の絞り深さ(mm)は、真空成形機(ASANO(株)製)にて、開口部150 mmφの円筒状金型を使用し、金型ヒーター温度を260℃の温度に設定して、良好な成形が可能な最大絞り深さを測定した値である。

帯電防止性

装置として矢野商会(株)製スタチックオネストメータを用い、積層シートの帯電防止フィルム層表面へ10 kVの電荷を2分間印加し、該印加停止後、電圧が1/2に減衰するまでの時間を測定した。

## 【0035】(III) 実験例

## 実験例1~9及び比較例1~3

## (1) 低発泡エチレン重合体樹脂シート(低発泡シート)の成形

表1に示す配合組成で配合し、マスキロ社製90 mm径二軸押出機及びダイを用いて180℃の成形温度で押し出し、厚み1 mmの低発泡シートを成形した。次に、この低発泡シートの発泡倍率及び発泡セルの寸法の測定を行ない、その結果を表1に示す。

## (2) オレフィン系重合体組成物フィルム(帯電防止フィルム)の成形

表2に示す配合組成で配合し、イーガン社製65 mmφTダイ成形機を用いて230℃の成形温度で押し出し、厚み100 μmの帯電防止フィルムを成形した。

## (3) 積層シートの製造

上記低発泡シート及び帯電防止フィルムを表3に示す組み合わせで選定し、接着剤として東洋モートン社製アドコート305を使用し、装置モダン社製ドライラミネータを用いて50℃で圧着して積層シートを作った。

## (4) 真空成形

次に、この積層シートをASANO(株)製真空成形機(M330型)にかけ、真空成形して深絞りを行なった。発泡セルが破れたり、積層シートに穴が開いたりしないで、良好な深絞り成形ができる最大の深さを測定した。その結果を、積層シートの帯電防止性評価結果と共に表3に示す。

## 【0036】

## 【表1】

表1

		低発泡シート						
		A	B	C	D	E	F	G
配 合 組 成	樹脂 (重量部)							
	種類							
	LDPE	100	-	-	-	100	100	100
	EVA	-	100	-	-	-	-	-
	HDPE	-	-	100	-	-	-	-
	L-LDPE	-	-	-	100	-	-	-
	物性							
	MFR (g/10分)	4	0.5	0.6	0.8	4	4	0.3
	MT (g)	5	11	9	5	5	5	12
	Q値	6.2	5.5	5.6	7.0	6.2	6.2	6.0
評 価	発泡剤 (x100 重量部)							
	AA	5	5	5	5	-	-	30
	CS	-	-	-	-	7	-	-
評 価	発泡倍率 (倍)	1.5	1.5	1.5	1.5	1.7	1.0	7.0
	発泡セル寸法 (mm)	0.3	0.15	0.2	0.3	0.2	0	0.15

AA:アゾジカルボンアミド

CS:重炭酸ソーダ・クエン酸の1:1混合系

【0037】

【表2】

表2

配 合 組 成 (重量部)	帯電防止フィルム					
	a	b	c	d	e	f
樹脂						
HDPE	100	100	100	-	100	-
EPP	-	-	-	100	-	100
帯電防止剤						
グリセリン脂肪酸エステル	0.1	-	-	0.3	-	-
ポリグリセリン脂肪酸エステル	-	0.2	-	-	-	-
N,N-ビス(2-ヒドロキシエチル)脂肪酸アミン	-	-	0.1	-	-	-

【0038】

【表3】

表 3

		実 施 例								比較例			
		1	2	3	4	5	6	7	8	1	2	3	4
低発泡 シート	A	○	-	-	-	-	○	○	○	○	○	-	-
	B	-	○	-	-	-	-	-	-	-	-	-	-
	C	-	-	○	-	-	-	-	-	-	-	-	-
	D	-	-	-	○	-	-	-	-	-	-	-	-
	E	-	-	-	-	○	-	-	-	-	-	-	-
	F	-	-	-	-	-	-	-	-	-	-	○	-
	G	-	-	-	-	-	-	-	-	-	-	-	○
帯電防止 フィルム	a	○	○	○	○	○	-	-	-	-	-	○	○
	b	-	-	-	-	-	○	-	-	-	-	-	-
	c	-	-	-	-	-	-	○	-	-	-	-	-
	d	-	-	-	-	-	-	-	○	-	-	-	-
	e	-	-	-	-	-	-	-	-	○	-	-	-
	f	-	-	-	-	-	-	-	-	-	○	-	-
真空成形絞り 深さ (x10 mm)		13	15	13	13	15	13	13	13	13	13	-	3
帯電圧半減期 (秒)		5	5	5	5	5	*A	*A	*A	*B	*B	5	5

○：積層に使用したもの。

\*A：2秒以下    \*B：180秒以上

## 【0039】

【発明の効果】本発明の低発泡エチレン重合体樹脂積層帯電防止性シートは、適度な柔軟性を有する低発泡体層を有し、その発泡セルが微細で、その寸法が均一であるために、熱成形した際にも発泡セルが破れず、良好な発泡状態が維持されたまま、一方向に偏ることなく均等に深絞り成形ができることから高度な深絞り成形を行なう

ことができる。そして、出来上がった積層シート熱成形体においては、発泡セルが微細で、その寸法が均一で一定しており極めた美麗であり、帯電防止性能を有し、かつ緩衝性を有するので緩衝材を要さない。また、本発明の積層シートは、熱成形せずにそのままシートとして使用することもできる。

フロントページの続き

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(71)Applicant : POOREN KAGAKU SANGYO KK

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(72)Inventor : ARAI YASUHIKO

ONISHI AKINORI

ODAKA KAZUO

ABE KUNIHIRO

## (54) LOW FOAMED ETHYLENE POLYMER RESIN LAMINATED ANTISTATIC SHEET

(57)Abstract:

**PROBLEM TO BE SOLVED:** To impart antistatic capacity and cushioning properties and to perform good deep drawing by forming the title sheet from an ethylene polymer resin layer of which the foaming magnification is a specific value and an olefinic polymer compsn. wherein specific pts.wt. of an antistatic agent is contained in specific pts.wt. of an olefinic polymer.

**SOLUTION:** A low foamed ethylene polymer resin laminated conductive sheet is constituted of an A-layer and a B-layer. The A-layer is composed of a low foamed ethylene polymer resin sheet with a foaming magnification of 1.01-3 times obtained by kneading a foaming agent with an ethylene polymer resin with a melt flow rate of 0.1-10g/10min and melt tension of 2-20g in a molten state and extruding the kneaded matter. The B-layer is composed of an olefinic polymer compsn. sheet or film obtained by compounding 0.1-5 pts.wt. of an antistatic agent with 100 pts.wt. of an olefinic polymer and kneading the obtained compound in a molten state to extrude the same. The low foamed ethylene polymer resin sheet and the olefinic polymer compsn. sheet or film are bonded through an adhesive under pressure or thermally bonded under pressure to be integrally laminated.

## LEGAL STATUS

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**CLAIMS**

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[Claim(s)]

[Claim 1] The low foaming ethylene polymer resin laminating antistatic nature sheet characterized by expansion ratio consisting of an olefin system polymer constituent layer (B horizon) which contains an antistatic agent 0.1 – 5 weight sections to the ethylene polymer resin layer (A horizon) and the olefin system polymer 100 weight section which are 1.01 to 3 times.

[Claim 2] The sheet according to claim 1 whose ethylene polymer resin is what shows melt tensions [ 2–20g ] physical properties for the melt flow rate of 0.1–10g / 10 minutes.

[Claim 3] The sheet according to claim 1 whose ethylene polymer resin is what shows the physical properties of Q value 2–9.

[Claim 4] the line of the low consistency ethylene homopolymer with which ethylene polymer resin was manufactured by the high pressure process, an ethylene–vinylacetate copolymer and the high density ethylene homopolymer manufactured by the inside low voltage method, ethylene, and other alpha olefins — the sheet according to claim 1 which was chosen from copolymers and which is a kind at least.

[Claim 5] The sheet according to claim 1 whose average dimension of a foaming cel is 0.05–0.5mm.

[Claim 6] The sheet according to claim 1 whose thickness of 0.1–5mm and a B horizon the thickness of an A horizon is 20–2000 micrometers.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]**

**[0001]**

**[Field of the Invention]** This invention relates to the laminating sheet which has the antistatic engine performance and has buffer nature and a good deep-drawing moldability.

**[0002]**

**[Description of the Prior Art]** Various Plastic solids, such as a container manufactured in a thermoplastics sheet by thermoforming methods, such as a vacuum forming, pressure forming, a vacuum and pressure forming, and die pressing shaping, an inner case (GESU), a tray, and an underlay, are widely used from the comparatively cheap thing. However, there was a problem referred to as wanting to improve more if for it to be hard, for rigidity to be too large to use it in these Plastic solids, it to be divided and it to be easy to be injured, the feel when touching.

**[0003]** If it is easy to attach a blemish to the product which in the case of the sheet which specifically formed the crevice corresponding to the configuration of an article (for example, IC receipt case and the case for metal-can receipt) it is too hard and is contained, since it is easy to slide in cases for glassware receipt, such as ampul, cosmetics, and wine if it faces using it in if it being easy to drop glassware etc., the putt which touch the body, and it is too hard or easy to be injured [ in a face or a finger ] in the part broken the field for toys — etc. — there was a problem of \*\*. Therefore, the actual condition is that the paper sheet which carried out the laminating of the velvet cloth, the resin sheet of high foaming [ \*\*\*\* / considering as the cloth product into which cotton was put ], etc. are using it in the case of the above-mentioned example.

**[0004]** However, it is hard to take out a high-class feeling with paper, and there is a problem referred to as that a production process becomes complicated and serves as the cost high with a cloth product. Moreover, with the resin sheet of high foaming, it is inferior to recoverability when construction material is too hard in the case of form polystyrene and deforms into it for example. It is difficult to hold an early configuration, or there is a problem referred to as unsuitable for sheet thermoforming, there is a problem referred to as that deep-drawing sheet thermoforming uniform except that construction material is too hard when it is polypropylene foam, and good is not made, when it is foaming polyurethane, size enlargement cannot be carried out to a clear configuration, but there is a problem referred to as being unable to store the product to contain exactly.

**[0005]**

**[Problem(s) to be Solved by the Invention]** Then, although polyethylene foam is also considered as a resin sheet material of high foaming If a foaming cel tends to be torn, it is going to fabricate deep-drawing shaping and a drawing configuration vividly and it fabricates acutely in case thermoforming is performed even if it carries out sheet thermoforming, only using polyethylene foam Since a foaming cel will be torn if foam is extended strongly locally, shaping of a deep-drawing Plastic solid with a clear drawing configuration or a complicated drawing configuration cannot be performed as a matter of fact, but there is a problem referred to as that a good Plastic solid is not acquired.

**[0006]** Moreover, on the other hand, the product equipped with electronic parts or an electrical

part depending on the product contained by various Plastic solids, such as a container, an inner case (GESU), a tray, and an underlay, requires caution, for example especially in order to dislike static electricity. Therefore, although packing by the antistatic nature packing material is usually common, since the case where shock absorbing material is also needed outside is common, there is a problem referred to as complicated and uneconomical.

[0007] Therefore, this invention aims at offering the low foaming ethylene polymer resin laminating sheet which can perform deep-drawing shaping with a clear drawing configuration while the foaming condition had been maintained good while it has the antistatic engine performance and has buffer nature.

[0008]

[Means for Solving the Problem] As a result of repeating research wholeheartedly in view of the above-mentioned trouble, this invention persons acquire knowledge that the above-mentioned object can be attained with the laminating sheet which consists of a low foaming ethylene polymer resin layer of description [ \*\*\*\* ], and an antistatic nature olefin system polymer constituent layer, and come to complete this invention.

[0009] That is, this invention is a low foaming ethylene polymer resin laminating antistatic nature sheet characterized by expansion ratio consisting of an olefin system polymer constituent layer (B horizon) which contains an antistatic agent 0.1 – 5 weight sections to the ethylene polymer resin layer (A horizon) and the olefin system polymer 100 weight section which are 1.01 to 3 times.

[0010]

[Embodiment of the Invention]

[I] Raw material (1) Ethylene polymer resin (a) Seed As ethylene polymer resin which constitutes the above-mentioned A horizon of a kind this invention laminating sheet, the homopolymer of ethylene or ethylene can be made into main constituents, and a copolymer with this, other alpha olefins, and/or other partial saturation monomers can be mentioned. As the above-mentioned alpha olefin, the alpha olefin of 3–8 can be mentioned preferably about three to 12 carbon number of a propylene, butene–1, 3–methyl pentene –1, 4–methyl pentene –1, a hexene –1, and octene–1 grade, for example. Moreover, as a partial saturation monomer besides the above, vinylsilane, such as partial saturation aromatic series monomer; vinyltrimetoxysilane, such as vinyl ester; styrene, such as unsaturated carboxylic acid, such as an acrylic acid, a methacrylic acid, a methyl acrylate, a methyl methacrylate, and a maleic anhydride, or derivative; vinyl acetate of those, and butanoic acid vinyl, methyl styrene, and a divinylbenzene, and gamma–methacryloxypropyltrimethoxysilane, etc. can be mentioned, for example.

[0011] the line of the ethylene which uses as a principal component also in these the high density ethylene homopolymer manufactured by the low voltage method in copolymer; with the ethylene which uses as a principal component the low consistency ethylene homopolymer with which desirable ethylene polymer resin is manufactured with a high pressure process, and ethylene, vinyl acetate and an acrylic acid, acrylate, a methacrylic acid, methacrylate, etc., and ethylene from foaming nature or vacuum-forming nature, and other alpha olefins (a propylene, butene–1, a hexene –1, octene–1 grade) — a copolymer etc. be mentioned. these copolymers — duality — you may be a 3 yuan [ not only a copolymer but ] or more copolymer. the line of the low consistency ethylene homopolymer (LDPE) with which especially desirable ethylene polymer resin is manufactured with a high pressure process also in these, an ethylene–vinylacetate copolymer (EVA), the high density ethylene homopolymer (HDPE) manufactured by the inside low voltage method, ethylene, and other alpha olefins — it is a copolymer (L–LDPE). Although the range which is the most components is sufficient as ethylene unless the effectiveness of this invention is spoiled remarkably, as for the content in the inside of the ethylene polymer resin of the alpha olefin in the above-mentioned ethylene polymer resin, and/or other partial saturation monomers, especially generally, it is desirable that it is 15 or less % of the weight 30 or less % of the weight.

[0012] (b) object the physical properties of the sex above-mentioned ethylene polymer resin — MFR (melt flow rate) — general — 0.1–10g/ — it is still more preferably desirable especially 0.2–

preferably for 0.3–6g / 10 minutes for 10 minutes. furthermore, ethylene polymer resin — Q value (molecular weight distribution) — general — 2–9 — it is still more preferably desirable 3–8, and that it is 4–7 especially preferably. When the value of Above MFR is too low, there is an inclination for the surface gloss of foam to worsen, and on the other hand, when too high, there is an inclination for a mechanical strength to worsen. Moreover, when the value of MT is too low, there is an inclination it to become difficult to obtain the foam of a high scale factor, and on the other hand, when too high, there is an inclination for a foaming cel to become rude. When the value of Q value is too low, there is an inclination for vacuum-forming nature to fall, and on the other hand, when too high, there is an inclination for the impact strength of foam to worsen.

[0013] (2) As a foaming agent used for making foaming agent this ethylene polymer resin foam, if used for low foaming, it can be used regardless of a class, but even if it is chemistry foaming agents, such as an AZOJI carvone amide, a bicarbonate-od-soda citric acid, and bicarbonate od soda, it does not matter even if it is physical foaming agents, such as butane, a pentane, a hexane, and a butanol, for example. Those who rather use the above-mentioned chemistry foaming agent are desirable at the point that the capacity of optimum dose can be generated in low foaming. Especially the thing for which an AZOJI carvone amide is used also in these foaming agents is desirable. Moreover, these foaming agents can also be used together and used.

[0014] (3) As an olefin system polymer which constitutes the above-mentioned B horizon of an olefin system polymer this invention laminating sheet, about two to 12 carbon number of ethylene, a propylene, butene-1, 3-methyl pentene -1, 4-methyl pentene -1, a hexene -1, and octene-1 grade and the desirable copolymer of the homopolymer of the alpha olefin of 2–8 or these alpha olefin comrade's copolymer, and the alpha olefin which uses an alpha olefin as a principal component further and other partial saturation monomers can be mentioned. Here, as other partial saturation monomers, diene conjugation of vinylsilane; butadienes [, such as partial saturation aromatic series monomer; vinyltrimetoxysilane such as vinyl ester; styrene, such as unsaturated carboxylic acid such as an acrylic acid, a methacrylic acid, a methyl acrylate a methyl methacrylate, and a maleic anhydride, or derivative; vinyl acetate of those and butanoic acid vinyl, methyl styrene, and a divinylbenzene, and gamma-methacryloxypropyltrimethoxysilane, ], isoprene, ethylidene norbornene, dicyclopentadiene, 1, and 4-hexadiene etc. or non-conjugate etc. can be mentioned, for example. Moreover, the gestalt of a copolymer does not ask random, a block, or a graft.

[0015] Although this olefin system polymer does not ask the shape of the shape of resin, and rubber, its thing of the shape of points, such as a moldability and rigidity, to resin is desirable. A thing desirable especially is ethylene system polymer resin or propylene system polymer resin. Here, it is desirable to use the above-mentioned ethylene polymer resin as ethylene system polymer resin, and it can mention the crystalline copolymer of duality with the propylene which uses the crystalline homopolymer of a propylene, and a propylene as a principal component as propylene system polymer resin, other alpha olefins (ethylene, butene-1, etc.), or other partial saturation monomers, or 3 yuan or more.

[0016] (4) As an antistatic agent which is another [ which constitutes the above-mentioned B horizon of an antistatic-agent this invention laminating sheet ] component Ethylene glycol, a diethylene glycol, a glycerol, trimethylol propane, Polyhydric alcohol and lauric acids, such as a pen TAERI slit and sorbitol, Fatty acid ester with unsaturated fatty acid, such as saturated fatty acid, such as a palmitic acid and stearin acid, or oleic acid, and linolic acid, Ester, such as ester of the higher alcohol which the fatty acid ester or higher alcohol which esterified the polyethylene glycol with the fatty acid is made to react with an organic acid or this acid anhydride, and is obtained; The sulfate specific salt of higher alcohol, such as lauryl alcohol and MAKKOU alcohol, Sulfate salts like a sodium dodecylbenzenesulfonate salt, and sulfuric-acid sulfonates; Amines; polyamide resin, such as phosphate; polyoxyethylene alkylamine obtained by the reaction with higher alcohol, a phosphoric anhydride, or phosphorus oxychloride, The quarternary-ammonium-salt; betaines; amino acid like amides; lauryl trimethylammonium chloride, such as a polyamide amine and alkyl diethanolamide; compounds of \*\*, such as an ethyleneoxide

acid ester, polyoxyethylene alkylamine, alkyl diethanolamide, and these concomitant use are desirable.

[0017] (5) In addition, into the ethylene polymer resin which constitutes the laminating sheet of arbitration component this invention, and/or an olefin system polymer, other arbitration components can be blended in the range which does not spoil the effectiveness of this invention remarkably in addition to the above-mentioned indispensable component. the object of adjustments as this arbitration component, such as physical properties and an appearance, — it is — an elastomer component and other resinous principles — or An antioxidant, a thermostabilizer, light stabilizer, a coloring agent, a conductive grant agent, an antimicrobial agent, An antifungal agent, a rust-proofer, a cellular regulator (foaming accelerator), a foaming agent decomposition temperature regulator, Various additive components, such as a neutralizer, a dispersant, molecular-weight regulators (radical generating agent etc.), a cross linking agent, a bridge formation assistant, a nucleating agent, a bulking agent, lubricant, a flame retarder, a fire-resistant assistant, processing aid, a heavy-metal deactivator, a plasticizer, a fluorescent brightener, a release agent, a softener, and a gloss grant agent, etc. can be mentioned.

[0018] [II] Although various approaches are employable in order to manufacture the laminating sheet of manufacture this invention of a laminating sheet, generally, other arbitration components are blended with the above-mentioned ethylene polymer resin by the foaming agent and the case, melting kneading is carried out, this is extruded first, and a low foaming ethylene polymer resin sheet (low foaming sheet: it becomes an A horizon) is manufactured.

Independently, other arbitration components are blended with the above-mentioned olefin system polymer by the antistatic agent and the case, melting kneading is carried out, this is extruded, and an olefin system polymer constituent sheet or a film (an antistatic sheet or a film: it becomes a B horizon) is manufactured. A laminating is carried out by heat welding, without using suitable adhesives for both these low foaming sheet, antistatic sheet, or film, or using adhesives. At this time, both or one of the two of these sheets or a film may be in a melting condition, and can also do a laminating by the co-extruding method.

[0019] (1) To the manufacture ethylene polymer resin of a low foaming ethylene polymer resin sheet Generally a foaming agent is preferably blended at 0.02 – 0.07% of the weight of a rate especially preferably 0.02 to 0.1% of the weight 0.01 to 0.2% of the weight, and they are the usual kneading extruder, for example, a 1 shaft extruder, a twin screw extruder, etc. about these. Generally resin temperature 170–240 degrees C by carrying out melting kneading under 180–230-degree C temperature conditions preferably, and extruding from the slit of a die It can be made to be able to foam 1.3 to 1.8 times preferably, and, generally thickness can manufacture a 0.2–3mm low foaming ethylene polymer resin sheet (low foaming sheet) one 1.01 to 3 times the expansion ratio of this preferably 0.1–5mm especially 1.1 to twice. This sheet is obtained as a low foaming sheet non-constructing a bridge.

[0020] If the above-mentioned expansion ratio is too low, while the thing inferior to flexibility is made, beautiful size enlargement may not be made in the following thermoforming process. On the other hand, if expansion ratio is too high, in the following thermoforming process, shaping will serve as a defect. Since the low foaming sheet obtained here can be fabricated without \*\*\*\*\*ing while the foaming condition had been maintained good at the time of the after-mentioned thermoforming, it can fabricate a drawing configuration vividly and is desirable.

[0021] Although many foaming cels arise in a low foaming sheet with the above-mentioned shaping In the low foaming sheet used by this invention, this foaming cel is detailed, and they are uniform. Generally the average dimension of this foaming cel preferably 0.05–0.5mm 0.1–0.4mm, Since a drawing configuration can be vividly sent while the foaming cel was hard to be destroyed and the foaming condition had been maintained good, also when the after-mentioned thermoforming of what is within the limits of 0.15–0.3mm preferably especially was carried out, it is desirable. Such an average dimension of a foaming cel can be prepared by choosing suitably the class of foaming agent, its amount, and the conditions at the time of the combination.

[0022] (2) To an olefin system polymer constituent sheet or the manufacture olefin system polymer of a film the 100 weight section — receiving — general — 0.1 – 5 weight section —

preferably, carrying out melting kneading of these with the usual kneading extruder, for example, a 1 shaft extruder, a twin screw extruder, etc., and extruding from the slit of a die especially Generally thickness can manufacture preferably 20–2000 micrometers of the olefin system polymer constituent sheets or films (the antistatic sheet or film) of 30–1500-micrometer antistatic nature suitably. Since shock resistance also falls outside it cannot give a static-free function, without obtaining satisfactory antistatic nature if there are too few above-mentioned antistatic agents, but a moldability will get worse on the other hand if many [ too ], and a shaping appearance worsens, it is not desirable.

[0023] (3) Product You may depend on the so-called dry laminate method which sticks by pressure and carries out a laminating with a roll etc. through suitable adhesives, for example, the 2 liquid hardening mold urethane system adhesives of a solvent mold, urethane emulsion system aqueous adhesives, etc., and in order to carry out the laminating of the layer above-mentioned low foaming sheet, an antistatic sheet, or the film, without using adhesives, thermocompression bonding of a low foaming sheet, an antistatic sheet, or the film may be carried out, melting unification may be carried out and it may carry out a laminating. Furthermore, therefore, a laminating may be carried out to the so-called co-extruding method which both a low foaming sheet, an antistatic sheet, a film, or one of the two is made to meet in the state of melting, and does a laminating. By the co-extruding method, it is especially easy to carry out accommodation of thickness, and since it is also economical, it is desirable. In addition, whether it is three layers as long as two-layer [ these ] is constituted since it is characterized by consisting of two-layer [ these ], or the laminating sheet in the invention in this application is a laminating with other base materials, it is not cared about, for example, may carry out the laminating of an antistatic sheet or the film to both sides of a low foaming sheet, or may carry out the laminating of cloth, the resin film, etc. further.

[0024] [III] The layered product with the thermoforming above-mentioned low foaming sheet layer (A horizon), an antistatic sheet, or a film layer (B horizon) It is in the condition which it was heated by various thermoforming methods, such as a vacuum-forming method shown below suitably, a pressure-forming method, a vacuum and a pressure-forming method, and the die pressing fabricating method, and was softened. After applying external force to this with means, such as a vacuum or application of pressure, making it deform into it and carrying out size enlargement to various configurations, the sheet thermoforming object of the various objects is acquired by cooling.

[0025] (1) After using either a female mold or a male and carrying out heating softening of the laminating sheet as a vacuum-forming method above-mentioned vacuum-forming method, it is the approach of carrying on a mold, making the gap of this sheet and a mold a vacuum, making stick a laminating sheet on the surface of a mold, and cooling and fabricating. Specifically, it is employable in various kinds of shaping approaches that straight shaping, drape forming, plug-assist-forming, plug assist reverse draw shaping, air slip shaping, snapback shaping, reverse draw shaping, plug assist air slip shaping, free shaping, and match mould shaping, plug ring shaping, slip shaping, contact hot forming, etc. are well-known.

[0026] (2) It is the approach of sticking to a mold the laminating sheet which carried out heating softening by the compressed air instead of the above-mentioned vacuum forming using atmospheric pressure as the pressure-forming method above-mentioned pressure forming by pressure, and fabricating it.

(3) It is the approach of fabricating combining the above-mentioned vacuum forming and pressure forming as a vacuum, the pressure-forming method above-mentioned vacuum, and a pressure-forming method.

(4) It is the approach of inserting the laminating sheet which carried out heating softening between up-and-down benches as a die pressing fabricating method above-mentioned die pressing fabricating method, and making press the approach of pushing and fabricating, or a laminating sheet with the mold heated as it was, and fabricating it in a mold.

The above-mentioned thermoforming is performed by usual thermoforming equipment according to a conventional method.

extracted even to a depth of 30mm or more so that a drawing configuration may come out vividly, maintaining a foaming condition good in thermoforming of a sheet to general deep drawing ] in the laminating sheet of this invention, deep-drawing shaping can be carried out especially preferably 40mm or more preferably 30mm or more even at the depth of 50mm or more \*\*. Mostly, the include angle of right-angle extent, and since it can bend and fabricate even to an inverse tapered shape extremely, this deep-drawing shaping can fabricate a drawing configuration for the wall surface by which deep drawing was carried out to this sheet surface vividly. At this time, that advanced deep-drawing shaping can be performed has a detailed foaming cel, and what is because deep-drawing shaping can be uniformly performed, without inclining toward an one direction while a foaming cel was not torn also when thermoforming was carried out but the good foaming condition had been maintained, since that dimension was uniform is presumed. Like this invention, it was unexpected by using the above-mentioned laminating sheet as a thermoforming ingredient that the above deep-drawing shaping was attained. In addition, this invention of it being applicable also to the Plastic solid which is not extracted in thermoforming is natural.

[0028] (5) \*\* the thermoforming object by which thermoforming was carried out to \*\*\*\*\* various configurations is agreed for various applications — as — judging — thermoforming — although separated from a laminating sheet on board, generally it is carried out by the approach of piercing with a decision cutting edge. When minute amount addition of what is usually beforehand used as an antiblocking agent of polyolefine into said ethylene polymer resin raw material at this time is carried out, the cutting-edge detached building at the time of decision is good, and since punching nature becomes good, it is desirable.

[0029] [IV] the application of a laminating sheet thermoforming object — in the thermoforming object which consists of a laminating sheet of such this invention, since deep-drawing shaping of the big depth can be given, it can fabricate on the various thermoforming objects applied to various applications. As an application of this thermoforming object, antistatic nature receipt cases, such as IC, a printed-circuit board, electronic parts, a precision machinery component, and various products that dislike dust, can be mentioned, for example.

[0030]

[Example] The example of an experiment shown below explains this invention still more concretely.

[I] Raw material (1) A horizon Ethylene polymer LDPE(high voltage low consistency ethylene homopolymer):MFR4g / 10 minutes to constitute, MT5g, Q value 6.2LDPE(high voltage low consistency ethylene homopolymer):MFR0.3g / 10 minutes, MT12g, Q value 6.0EVA(ethylene-vinylacetate copolymer):MFR0.5g / 10 minutes, MT11g, Q value 5.5HDPE(high density ethylene homopolymer):MFR0.6g / 10 minutes, MT9g, Q value 5.6 L-LDPE(copolymer of ethylene and 7% of the weight of butene-1):MFR0.8g / 10 minutes, MT5g, Q value 7.0 [0031] (2) Foaming agent AA : AZOJI carvone amide CS : 1:1 mixed stock of a bicarbonate-od-soda citric acid [0032] (3) Olefin system polymer HDPE(high density ethylene homopolymer):MFR0.6g/10 minute EPP (propylene ethylene block copolymer):MFR33g / 60 % of the weight (4) of 12 % of the weight [ of 10 minutes (230 degrees-C, 2.16kgf load) : 23-degree-C xylene extractives ] : propylene contents in the above-mentioned extractives which constitute a B horizon Antistatic-agent glycerine fatty acid ester: The Kao Corp. make, trade name "electro stripper TS-5" Polyglyceryl fatty acid ester: The LION make, a trade name "AMO stat DGS" N[ N and ]-screw (2-hydroxyethyl) fatty-acid amine: The LION make, a trade name "AMO stat 310"

[0033] [II] The assessment approach (1) A resin physical-properties MFR melt flow rate (MFR) is JIS. It is the value measured by the temperature of 190 degrees C, and load 2.16kgf according to a convention of K7210.

M T melt tension (MT) is the value which extruded at a part for melting drop speed 10mm/, and the temperature of 190 degrees C, and was measured by part for taking over speed 4m/using KYAPI Good rough Made from an Oriental energy machine.

Q Value Q value (molecular weight distribution) is a value measured with gel permeation

[0034] (2) Criticism \*\*\*\*\* expansion ratio is the value which measured the consistency foaming before and after foaming using the pycnometer, and \*(ed) by the consistency after foaming in the consistency before foaming.

The average dimension of a foaming cel dimension foaming cel is the value which carried out amplification fluoroscopy of the thickness direction and the field sliced in parallel of foam using the microscope, and measured the average dimension of air bubbles.

The drawing depth (mm) of a drawing depth Plastic solid is the value which used the cylindrical metal mold of 150mm of openings phi, set metal mold heater temperature as the temperature of 260 degrees C, and measured the maximum drawing depth in which good shaping is possible with the vacuum forming machine (product made from ASANO).

Using the Shishido Company static ONESUTO meter as antistatic nature equipment, the 10kV charge was impressed for 2 minutes to the antistatic film layer front face of a laminating sheet, and time amount until an electrical potential difference declines to one half was measured after this impression halt.

[0035] [III] The example examples 1–9 of an experiment, and examples 1–3 of a comparison (1) It blended by the combination presentation shown in the shaping table 1 of a low foaming ethylene polymer resin sheet (low foaming sheet), and extruded with the molding temperature of 180 degrees C using the diameter twin screw extruder of 90mm by the mass clo company, and the die, and the low foaming sheet with a thickness of 1mm was fabricated. Next, the expansion ratio of this low foaming sheet and the dimension of a foaming cel are measured, and that result is shown in a table 1.

(2) It blended by the combination presentation shown in the shaping table 2 of an olefin system polymer constituent film (antistatic film), and extruded with the molding temperature of 230 degrees C using the Eagan 65mmphi T–die making machine, and the antistatic film with a thickness of 100 micrometers was fabricated.

(3) It selected in the combination which shows the manufacture above–mentioned low foaming sheet and antistatic film of a laminating sheet in a table 3, Oriental Morton ADOKOTO 305 was used as adhesives, it was stuck by pressure at 50 degrees C using the dry laminator by the equipment modern company, and the laminating sheet was made.

(4) The vacuum forming of a vacuum forming, next this laminating sheet was covered and carried out to the vacuum forming machine made from ASANO (M330 mold), and deep drawing was performed. The greatest depth which can perform good deep–drawing shaping was measured without having torn the foaming cel or a hole's opening on a laminating sheet. The result is shown in a table 3 with the antistatic nature assessment result of a laminating sheet.

[0036]

[A table 1]

表 1

		低発泡シート						
		A	B	C	D	E	F	G
配 合 組 成	樹脂 (重量部)							
	種類							
	LDPE	100	-	-	-	100	100	100
	EVA	-	100	-	-	-	-	-
	HDPE	-	-	100	-	-	-	-
	L-LDPE	-	-	-	100	-	-	-
	物性							
	MFR (g/10分)	4	0.5	0.6	0.8	4	4	0.3
	MT (g)	5	11	9	5	5	5	12
	Q値	6.2	5.5	5.6	7.0	6.2	6.2	6.0
	発泡剤 (x100 重量部)							
	AA	5	5	5	5	-	-	30
	CS	-	-	-	-	7	-	-
評 価	発泡倍率 (倍)	1.5	1.5	1.5	1.5	1.7	1.0	7.0
	発泡セル寸法 (mm)	0.3	0.15	0.2	0.3	0.2	0	0.15

AA : アゾジカルボンアミド

CS : 重炭酸ソーダ・クエン酸の 1 : 1 混合系

[0037]

[A table 2]

表 2

配 合 組 成 (重量部)	帯電防止フィルム					
	a	b	c	d	e	f
樹脂						
HDPE	100	100	100	-	100	-
EPP	-	-	-	100	-	100
帯電防止剤						
グリセリン脂肪酸エステル	0.1	-	-	0.3	-	-
ポリグリセリン脂肪酸エステル	-	0.2	-	-	-	-
N,N-ビス(2-ヒドロキシエチル)脂肪族アミン	-	-	0.1	-	-	-

[0038]

[A table 3]

表 3

		実 施 例								比 較 例			
		1	2	3	4	5	6	7	8	1	2	3	4
低発泡 シート	A	○	-	-	-	-	○	○	○	○	○	-	-
	B	-	○	-	-	-	-	-	-	-	-	-	-
	C	-	-	○	-	-	-	-	-	-	-	-	-
	D	-	-	-	○	-	-	-	-	-	-	-	-
	E	-	-	-	-	○	-	-	-	-	-	-	-
	F	-	-	-	-	-	-	-	-	-	-	○	-
	G	-	-	-	-	-	-	-	-	-	-	-	○
帯電防止 フィルム	a	○	○	○	○	○	-	-	-	-	-	○	○
	b	-	-	-	-	-	○	-	-	-	-	-	-
	c	-	-	-	-	-	-	○	-	-	-	-	-
	d	-	-	-	-	-	-	-	○	-	-	-	-
	e	-	-	-	-	-	-	-	-	○	-	-	-
	f	-	-	-	-	-	-	-	-	-	○	-	-
真空成形絞り 深さ (x10 mm)		13	15	13	13	15	13	13	13	13	13	-	3
帯電圧半減期 (秒)		5	5	5	5	5	*A	*A	*A	*B	*B	5	5

○：積層に使用したもの。

\*A：2秒以下    \*B：180秒以上

[0039]

[Effect of the Invention] The low foaming ethylene polymer resin laminating antistatic nature sheet of this invention has the low foam layer which has moderate flexibility, the foaming cel is detailed, and while a foaming cel was not torn also when thermoforming was carried out, since the dimension was uniform, but the good foaming condition had been maintained, it can perform advanced deep-drawing shaping from the ability of deep-drawing shaping to be performed uniformly, without inclining toward an one direction. And in the done laminating sheet thermoforming object, a foaming cel is detailed, and since the dimension is uniform and it is fixed, and it reached to an extreme and is beautiful, and it has the antistatic engine performance and it has buffer nature, there is no \*\*\*\* about shock absorbing material. Moreover, the laminating sheet of this invention can also be used as a sheet as it is, without carrying out thermoforming.

[Translation done.]

**\* NOTICES \***

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**TECHNICAL FIELD**

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[Field of the Invention] This invention relates to the laminating sheet which has the antistatic engine performance and has buffer nature and a good deep-drawing moldability.

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**PRIOR ART**

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[Description of the Prior Art] Various Plastic solids, such as a container manufactured in a thermoplastics sheet by thermoforming methods, such as a vacuum forming, pressure forming, a vacuum and pressure forming, and die pressing shaping, an inner case (GESU), a tray, and an underlay, are widely used from the comparatively cheap thing. However, there was a problem referred to as wanting to improve more if for it to be hard, for rigidity to be too large to use it in these Plastic solids, it to be divided and it to be easy to be injured, the feel when touching.

[0003] If it is easy to attach a blemish to the product which in the case of the sheet which specifically formed the crevice corresponding to the configuration of an article (for example, IC receipt case and the case for metal-can receipt) it is too hard and is contained, since it is easy to slide in cases for glassware receipt, such as ampul, cosmetics, and wine if it faces using it in if it being easy to drop glassware etc., the putt which touch the body, and it is too hard or easy to be injured [ in a face or a finger ] in the part broken the field for toys — etc. — there was a problem of \*\*. Therefore, the actual condition is that the paper sheet which carried out the laminating of the velvet cloth, the resin sheet of high foaming [ \*\*\*\* / considering as the cloth product into which cotton was put ], etc. are using it in the case of the above-mentioned example.

[0004] However, it is hard to take out a high-class feeling with paper, and there is a problem referred to as that a production process becomes complicated and serves as the cost high with a cloth product. Moreover, with the resin sheet of high foaming, it is inferior to recoverability when construction material is too hard in the case of form polystyrene and deforms into it for example. It is difficult to hold an early configuration, or there is a problem referred to as unsuitable for sheet thermoforming, there is a problem referred to as that deep-drawing sheet thermoforming uniform except that construction material is too hard when it is polypropylene foam, and good is not made, when it is foaming polyurethane, size enlargement cannot be carried out to a clear configuration, but there is a problem referred to as being unable to store the product to contain exactly.

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**EFFECT OF THE INVENTION**

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[Effect of the Invention] The low foaming ethylene polymer resin laminating antistatic nature sheet of this invention has the low foam layer which has moderate flexibility, the foaming cel is detailed, and while a foaming cel was not torn also when thermoforming was carried out, since the dimension was uniform, but the good foaming condition had been maintained, it can perform advanced deep-drawing shaping from the ability of deep-drawing shaping to be performed uniformly, without inclining toward an one direction. And in the done laminating sheet thermoforming object, a foaming cel is detailed, and since the dimension is uniform and it is fixed, and it reached to an extreme and is beautiful, and it has the antistatic engine performance and it has buffer nature, there is no \*\*\*\* about shock absorbing material. Moreover, the laminating sheet of this invention can also be used as a sheet as it is, without carrying out thermoforming.

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention] Then, although polyethylene foam is also considered as a resin sheet material of high foaming. If a foaming cell tends to be torn, it is going to fabricate deep-drawing shaping and a drawing configuration vividly and it fabricates acutely in case thermoforming is performed even if it carries out sheet thermoforming, only using polyethylene foam. Since a foaming cell will be torn if foam is extended strongly locally, shaping of a deep-drawing Plastic solid with a clear drawing configuration or a complicated drawing configuration cannot be performed as a matter of fact, but there is a problem referred to as that a good Plastic solid is not acquired.

[0006] Moreover, on the other hand, the product equipped with electronic parts or an electrical part depending on the product contained by various Plastic solids, such as a container, an inner case (GESU), a tray, and an underlay, requires caution, for example especially in order to dislike static electricity. Therefore, although packing by the antistatic nature packing material is usually common, since the case where shock absorbing material is also needed outside is common, there is a problem referred to as complicated and uneconomical.

[0007] Therefore, this invention aims at offering the low foaming ethylene polymer resin laminating sheet which can perform deep-drawing shaping with a clear drawing configuration while the foaming condition had been maintained good while it has the antistatic engine performance and has buffer nature.

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**MEANS**

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[Means for Solving the Problem] As a result of repeating research wholeheartedly in view of the above-mentioned trouble, this invention persons acquire knowledge that the above-mentioned object can be attained with the laminating sheet which consists of a low foaming ethylene polymer resin layer of description [ \*\*\*\* ], and an antistatic nature olefin system polymer constituent layer, and come to complete this invention.

[0009] That is, this invention is a low foaming ethylene polymer resin laminating antistatic nature sheet characterized by expansion ratio consisting of an olefin system polymer constituent layer (B horizon) which contains an antistatic agent 0.1 – 5 weight sections to the ethylene polymer resin layer (A horizon) and the olefin system polymer 100 weight section which are 1.01 to 3 times.

[0010]

[Embodiment of the Invention]

[I] Raw material (1) Ethylene polymer resin (a) Seed As ethylene polymer resin which constitutes the above-mentioned A horizon of a kind this invention laminating sheet, the homopolymer of ethylene or ethylene can be made into main constituents, and a copolymer with this, other alpha olefins, and/or other partial saturation monomers can be mentioned. As the above-mentioned alpha olefin, the alpha olefin of 3–8 can be mentioned preferably about three to 12 carbon number of a propylene, butene–1, 3–methyl pentene –1, 4–methyl pentene –1, a hexene –1, and octene–1 grade, for example. Moreover, as a partial saturation monomer besides the above, vinylsilane, such as partial saturation aromatic series monomer; vinyltrimetoxysilane, such as vinyl ester; styrene, such as unsaturated carboxylic acid, such as an acrylic acid, a methacrylic acid, a methyl acrylate, a methyl methacrylate, and a maleic anhydride, or derivative; vinyl acetate of those, and butanoic acid vinyl, methyl styrene, and a divinylbenzene, and gamma–methacryloxypropyltrimethoxysilane, etc. can be mentioned, for example.

[0011] the line of the ethylene which uses as a principal component also in these the high density ethylene homopolymer manufactured by the low voltage method in copolymer; with the ethylene which uses as a principal component the low consistency ethylene homopolymer with which desirable ethylene polymer resin is manufactured with a high pressure process, and ethylene, vinyl acetate and an acrylic acid, acrylate, a methacrylic acid, methacrylate, etc., and ethylene from foaming nature or vacuum-forming nature, and other alpha olefins (a propylene, butene–1, a hexene –1, octene–1 grade) — a copolymer etc. be mentioned. these copolymers — duality — you may be a 3 yuan [ not only a copolymer but ] or more copolymer. the line of the low consistency ethylene homopolymer (LDPE) with which especially desirable ethylene polymer resin is manufactured with a high pressure process also in these, an ethylene–vinylacetate copolymer (EVA), the high density ethylene homopolymer (HDPE) manufactured by the inside low voltage method, ethylene, and other alpha olefins — it is a copolymer (L–LDPE). Although the range which is the most components is sufficient as ethylene unless the effectiveness of this invention is spoiled remarkably, as for the content in the inside of the ethylene polymer resin of the alpha olefin in the above-mentioned ethylene polymer resin, and/or other partial saturation monomers, especially generally, it is desirable that it is 15 or less % of the weight 30 or less % of

[0012] (b) object the physical properties of the sex above-mentioned ethylene polymer resin — MFR (melt flow rate) — general — 0.1–10g/ — it is still more preferably desirable especially 0.2–8g / that 2–20g (melt tension) of 3–16g of MT is generally 4–12g especially preferably still more preferably for 0.3–6g / 10 minutes for 10 minutes for 10 minutes. furthermore, ethylene polymer resin — Q value (molecular weight distribution) — general — 2–9 — it is still more preferably desirable 3–8, and that it is 4–7 especially preferably. When the value of Above MFR is too low, there is an inclination for the surface gloss of foam to worsen, and on the other hand, when too high, there is an inclination for a mechanical strength to worsen. Moreover, when the value of MT is too low, there is an inclination it to become difficult to obtain the foam of a high scale factor, and on the other hand, when too high, there is an inclination for a foaming cel to become rude. When the value of Q value is too low, there is an inclination for vacuum-forming nature to fall, and on the other hand, when too high, there is an inclination for the impact strength of foam to worsen.

[0013] (2) As a foaming agent used for making foaming agent this ethylene polymer resin foam, if used for low foaming, it can be used regardless of a class, but even if it is chemistry foaming agents, such as an AZOJI carvone amide, a bicarbonate-od-soda citric acid, and bicarbonate od soda, it does not matter even if it is physical foaming agents, such as butane, a pentane, a hexane, and a butanol, for example. Those who rather use the above-mentioned chemistry foaming agent are desirable at the point that the capacity of optimum dose can be generated in low foaming. Especially the thing for which an AZOJI carvone amide is used also in these foaming agents is desirable. Moreover, these foaming agents can also be used together and used.

[0014] (3) As an olefin system polymer which constitutes the above-mentioned B horizon of an olefin system polymer this invention laminating sheet, about two to 12 carbon number of ethylene, a propylene, butene-1, 3-methyl pentene -1, 4-methyl pentene -1, a hexene -1, and octene-1 grade and the desirable copolymer of the homopolymer of the alpha olefin of 2-8 or these alpha olefin comrade's copolymer, and the alpha olefin which uses an alpha olefin as a principal component further and other partial saturation monomers can be mentioned. Here, as other partial saturation monomers, diene conjugation of vinylsilane; butadienes [, such as partial saturation aromatic series monomer; vinyltrimetoxysilane such as vinyl ester; styrene, such as unsaturated carboxylic acid such as an acrylic acid, a methacrylic acid, a methyl acrylate a methyl methacrylate, and a maleic anhydride, or derivative; vinyl acetate of those and butanoic acid vinyl, methyl styrene, and a divinylbenzene, and gamma-methacryloxypropyltrimethoxysilane, ], isoprene, ethylidene norbornene, dicyclopentadiene, 1, and 4-hexadiene etc. or non-conjugate etc. can be mentioned, for example. Moreover, the gestalt of a copolymer does not ask random, a block, or a graft.

[0015] Although this olefin system polymer does not ask the shape of the shape of resin, and rubber, its thing of the shape of points, such as a moldability and rigidity, to resin is desirable. A thing desirable especially is ethylene system polymer resin or propylene system polymer resin. Here, it is desirable to use the above-mentioned ethylene polymer resin as ethylene system polymer resin, and it can mention the crystalline copolymer of duality with the propylene which uses the crystalline homopolymer of a propylene, and a propylene as a principal component as propylene system polymer resin, other alpha olefins (ethylene, butene-1, etc.), or other partial saturation monomers, or 3 yuan or more.

[0016] (4) As an antistatic agent which is another [ which constitutes the above-mentioned B horizon of an antistatic-agent this invention laminating sheet ] component Ethylene glycol, a diethylene glycol, a glycerol, trimethylol propane, Polyhydric alcohol and lauric acids, such as a pen TAERI slit and sorbitol, Fatty acid ester with unsaturated fatty acid, such as saturated fatty acid, such as a palmitic acid and stearin acid, or oleic acid, and linolic acid, Ester, such as ester of the higher alcohol which the fatty acid ester or higher alcohol which esterified the polyethylene glycol with the fatty acid is made to react with an organic acid or this acid anhydride, and is obtained; The sulfate specific salt of higher alcohol, such as lauryl alcohol and MAKKOU alcohol, Sulfate salts like a sodium dodecylbenzenesulfonate salt, and sulfuric-acid sulfonates; Amines; polyamide resin, such as phosphate; polyoxyethylene alkylamine obtained by

quarternary-ammonium-salt; betaines; amino acid like amides; lauryl trimethylammonium chloride, such as a polyamide amine and alkyl diethanolamide; compounds of \*\*, such as an ethyleneoxide addition product, can be mentioned. Especially, a glycerine fatty acid ester, polyglyceryl fatty acid ester, polyoxyethylene alkylamine, alkyl diethanolamide, and these concomitant use are desirable.

[0017] (5) In addition, into the ethylene polymer resin which constitutes the laminating sheet of arbitration component this invention, and/or an olefin system polymer, other arbitration components can be blended in the range which does not spoil the effectiveness of this invention remarkably in addition to the above-mentioned indispensable component. the object of adjustments as this arbitration component, such as physical properties and an appearance, — it is — an elastomer component and other resinous principles — or An antioxidant, a thermostabilizer, light stabilizer, a coloring agent, a conductive grant agent, an antimicrobial agent, An antifungal agent, a rusr-proofer, a cellular regulator (foaming accelerator), a foaming agent decomposition temperature regulator, Various additive components, such as a neutralizer, a dispersant, molecular-weight regulators (radical generating agent etc.), a cross linking agent, a bridge formation assistant, a nucleating agent, a bulking agent, lubricant, a flame retarder, a fire-resistant assistant, processing aid, a heavy-metal deactivator, a plasticizer, a fluorescent brightener, a release agent, a softener, and a gloss grant agent, etc. can be mentioned.

[0018] [II] Although various approaches are employable in order to manufacture the laminating sheet of manufacture this invention of a laminating sheet, generally, other arbitration components are blended with the above-mentioned ethylene polymer resin by the foaming agent and the case, melting kneading is carried out, this is extruded first, and a low foaming ethylene polymer resin sheet (low foaming sheet: it becomes an A horizon) is manufactured.

Independently, other arbitration components are blended with the above-mentioned olefin system polymer by the antistatic agent and the case, melting kneading is carried out, this is extruded, and an olefin system polymer constituent sheet or a film (an antistatic sheet or a film: it becomes a B horizon) is manufactured. A laminating is carried out by heat welding, without using suitable adhesives for both these low foaming sheet, antistatic sheet, or film, or using adhesives. At this time, both or one of the two of these sheets or a film may be in a melting condition, and can also do a laminating by the co-extruding method.

[0019] (1) To the manufacture ethylene polymer resin of a low foaming ethylene polymer resin sheet Generally a foaming agent is preferably blended at 0.02 – 0.07% of the weight of a rate especially preferably 0.02 to 0.1% of the weight 0.01 to 0.2% of the weight, and they are the usual kneading extruder, for example, a 1 shaft extruder, a twin screw extruder, etc. about these. Generally resin temperature 170–240 degrees C by carrying out melting kneading under 180–230-degree C temperature conditions preferably, and extruding from the slit of a die It can be made to be able to foam 1.3 to 1.8 times preferably, and, generally thickness can manufacture a 0.2–3mm low foaming ethylene polymer resin sheet (low foaming sheet) one 1.01 to 3 times the expansion ratio of this preferably 0.1–5mm especially 1.1 to twice. This sheet is obtained as a low foaming sheet non-constructing a bridge.

[0020] If the above-mentioned expansion ratio is too low, while the thing inferior to flexibility is made, beautiful size enlargement may not be made in the following thermoforming process. On the other hand, if expansion ratio is too high, in the following thermoforming process, shaping will serve as a defect. Since the low foaming sheet obtained here can be fabricated without \*\*\*\*\*ing while the foaming condition had been maintained good at the time of the after-mentioned thermoforming, it can fabricate a drawing configuration vividly and is desirable.

[0021] Although many foaming cels arise in a low foaming sheet with the above-mentioned shaping In the low foaming sheet used by this invention, this foaming cel is detailed, and they are uniform. Generally the average dimension of this foaming cel preferably 0.05–0.5mm 0.1–0.4mm, Since a drawing configuration can be vividly sent while the foaming cel was hard to be destroyed and the foaming condition had been maintained good, also when the after-mentioned thermoforming of what is within the limits of 0.15–0.3mm preferably especially was carried out, it is desirable. Such an average dimension of a foaming cel can be prepared by choosing suitably

[0022] (2) To an olefin system polymer constituent sheet or the manufacture olefin system polymer of a film the 100 weight section — receiving — general — 0.1 – 5 weight section — desirable — 0.3 – 4 weight section — By blending the antistatic agent of 0.3 – 3 weight section preferably, carrying out melting kneading of these with the usual kneading extruder, for example, a 1 shaft extruder, a twin screw extruder, etc., and extruding from the slit of a die especially Generally thickness can manufacture preferably 20–2000 micrometers of the olefin system polymer constituent sheets or films (the antistatic sheet or film) of 30–1500–micrometer antistatic nature suitably. Since shock resistance also falls outside it cannot give a static-free function, without obtaining satisfactory antistatic nature if there are too few above-mentioned antistatic agents, but a moldability will get worse on the other hand if many [ too ], and a shaping appearance worsens, it is not desirable.

[0023] (3) Product You may depend on the so-called dry laminate method which sticks by pressure and carries out a laminating with a roll etc. through suitable adhesives, for example, the 2 liquid hardening mold urethane system adhesives of a solvent mold, urethane emulsion system aqueous adhesives, etc., and in order to carry out the laminating of the layer above-mentioned low foaming sheet, an antistatic sheet, or the film, without using adhesives, thermocompression bonding of a low foaming sheet, an antistatic sheet, or the film may be carried out, melting unification may be carried out and it may carry out a laminating. Furthermore, therefore, a laminating may be carried out to the so-called co-extruding method which both a low foaming sheet, an antistatic sheet, a film, or one of the two is made to meet in the state of melting, and does a laminating. By the co-extruding method, it is especially easy to carry out accommodation of thickness, and since it is also economical, it is desirable. In addition, whether it is three layers as long as two-layer [ these ] is constituted since it is characterized by consisting of two-layer [ these ], or the laminating sheet in the invention in this application is a laminating with other base materials, it is not cared about, for example, may carry out the laminating of an antistatic sheet or the film to both sides of a low foaming sheet, or may carry out the laminating of cloth, the resin film, etc. further.

[0024] [III] The layered product with the thermoforming above-mentioned low foaming sheet layer (A horizon), an antistatic sheet, or a film layer (B horizon) It is in the condition which it was heated by various thermoforming methods, such as a vacuum-forming method shown below suitably, a pressure-forming method, a vacuum and a pressure-forming method, and the die pressing fabricating method, and was softened. After applying external force to this with means, such as a vacuum or application of pressure, making it deform into it and carrying out size enlargement to various configurations, the sheet thermoforming object of the various objects is acquired by cooling.

[0025] (1) After using either a female mold or a male and carrying out heating softening of the laminating sheet as a vacuum-forming method above-mentioned vacuum-forming method, it is the approach of carrying on a mold, making the gap of this sheet and a mold a vacuum, making stick a laminating sheet on the surface of a mold, and cooling and fabricating. Specifically, it is employable in various kinds of shaping approaches that straight shaping, drape forming, plug-assist-forming, plug assist reverse draw shaping, air slip shaping, snapback shaping, reverse draw shaping, plug assist air slip shaping, free shaping, and match mould shaping, plug ring shaping, slip shaping, contact hot forming, etc. are well-known.

[0026] (2) It is the approach of sticking to a mold the laminating sheet which carried out heating softening by the compressed air instead of the above-mentioned vacuum forming using atmospheric pressure as the pressure-forming method above-mentioned pressure forming by pressure, and fabricating it.

(3) It is the approach of fabricating combining the above-mentioned vacuum forming and pressure forming as a vacuum, the pressure-forming method above-mentioned vacuum, and a pressure-forming method.

(4) It is the approach of inserting the laminating sheet which carried out heating softening between up-and-down benches as a die pressing fabricating method above-mentioned die pressing fabricating method, and making press the approach of pushing and fabricating, or a

The above-mentioned thermoforming is performed by usual thermoforming equipment according to a conventional method.

[0027] Also unexpectedly [ although it is difficult to perform deep-drawing shaping usually extracted even to a depth of 30mm or more so that a drawing configuration may come out vividly, maintaining a foaming condition good in thermoforming of a sheet to general deep drawing ] in the laminating sheet of this invention, deep-drawing shaping can be carried out especially preferably 40mm or more preferably 30mm or more even at the depth of 50mm or more \*\*. Mostly, the include angle of right-angle extent, and since it can bend and fabricate even to an inverse tapered shape extremely, this deep-drawing shaping can fabricate a drawing configuration for the wall surface by which deep drawing was carried out to this sheet surface vividly. At this time, that advanced deep-drawing shaping can be performed has a detailed foaming cel, and what is because deep-drawing shaping can be uniformly performed, without inclining toward an one direction while a foaming cel was not torn also when thermoforming was carried out but the good foaming condition had been maintained, since that dimension was uniform is presumed. Like this invention, it was unexpected by using the above-mentioned laminating sheet as a thermoforming ingredient that the above deep-drawing shaping was attained. In addition, this invention of it being applicable also to the Plastic solid which is not extracted in thermoforming is natural.

[0028] (5) \*\* the thermoforming object by which thermoforming was carried out to \*\*\*\*\* various configurations is agreed for various applications — as — judging — thermoforming — although separated from a laminating sheet on board, generally it is carried out by the approach of piercing with a decision cutting edge. When minute amount addition of what is usually beforehand used as an antiblocking agent of polyolefine into said ethylene polymer resin raw material at this time is carried out, the cutting-edge detached building at the time of decision is good, and since punching nature becomes good, it is desirable.

[0029] [IV] the application of a laminating sheet thermoforming object — in the thermoforming object which consists of a laminating sheet of such this invention, since deep-drawing shaping of the big depth can be given, it can fabricate on the various thermoforming objects applied to various applications. As an application of this thermoforming object, antistatic nature receipt cases, such as IC, a printed-circuit board, electronic parts, a precision machinery component, and various products that dislike dust, can be mentioned, for example.

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**EXAMPLE**

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[Example] The example of an experiment shown below explains this invention still more concretely.

[I] Raw material (1) A horizon Ethylene polymer LDPE (high voltage low consistency ethylene homopolymer): MFR 4g / 10 minutes to constitute, MT 5g, Q value 6.2 LDPE (high voltage low consistency ethylene homopolymer): MFR 0.3g / 10 minutes, MT 12g, Q value 6.0 EVA (ethylene-vinylacetate copolymer): MFR 0.5g / 10 minutes, MT 11g, Q value 5.5 HDPE (high density ethylene homopolymer): MFR 0.6g / 10 minutes, MT 9g, Q value 5.6 L-LDPE (copolymer of ethylene and 7% of the weight of butene-1): MFR 0.8g / 10 minutes, MT 5g, Q value 7.0 [0031] (2) Foaming agent AA : AZOJI carvone amide CS : 1:1 mixed stock of a bicarbonate-soda citric acid [0032] (3) Olefin system polymer HDPE (high density ethylene homopolymer): MFR 0.6g / 10 minute EPP (propylene ethylene block copolymer): MFR 33g / 60 % of the weight (4) of 12 % of the weight [ of 10 minutes (230 degrees-C, 2.16kgf load) : 23-degree-C xylene extractives ] : propylene contents in the above-mentioned extractives which constitute a B horizon Antistatic-agent glycerine fatty acid ester: The Kao Corp. make, trade name "electro stripper TS-5" Polyglyceryl fatty acid ester: The LION make, a trade name "AMO stat DGS" N[ N and ]-screw (2-hydroxyethyl) fatty-acid amine: The LION make, a trade name "AMO stat 310"

[0033] [II] The assessment approach (1) A resin physical-properties MFR melt flow rate (MFR) is JIS. It is the value measured by the temperature of 190 degrees C, and load 2.16kgf according to a convention of K7210.

M T melt tension (MT) is the value which extruded at a part for melting drop speed 10mm/, and the temperature of 190 degrees C, and was measured by part for taking over speed 4m/using KYAPI Good rough Made from an Oriental energy machine.

Q Value Q value (molecular weight distribution) is a value measured with gel permeation chromatography (GPC).

[0034] (2) Criticism \*\*\*\*\* expansion ratio is the value which measured the consistency foaming before and after foaming using the pycnometer, and \*\* (ed) by the consistency after foaming in the consistency before foaming.

The average dimension of a foaming cel dimension foaming cel is the value which carried out amplification fluoroscopy of the thickness direction and the field sliced in parallel of foam using the microscope, and measured the average dimension of air bubbles.

The drawing depth (mm) of a drawing depth Plastic solid is the value which used the cylindrical metal mold of 150mm of openings phi, set metal mold heater temperature as the temperature of 260 degrees C, and measured the maximum drawing depth in which good shaping is possible with the vacuum forming machine (product made from ASANO).

Using the Shishido Company static ONESUTO meter as antistatic nature equipment, the 10kV charge was impressed for 2 minutes to the antistatic film layer front face of a laminating sheet, and time amount until an electrical potential difference declines to one half was measured after this impression halt.

[0035] [III] The example examples 1-9 of an experiment, and examples 1-3 of a comparison (1) It blended by the combination presentation shown in the shaping table 1 of a low foaming ethylene

polymer resin sheet (low foaming sheet), and extruded with the molding temperature of 180 degrees C using the diameter twin screw extruder of 90mm by the mass clo company, and the die, and the low foaming sheet with a thickness of 1mm was fabricated. Next, the expansion ratio of this low foaming sheet and the dimension of a foaming cel are measured, and that result is shown in a table 1.

(2) It blended by the combination presentation shown in the shaping table 2 of an olefin system polymer constituent film (antistatic film), and extruded with the molding temperature of 230 degrees C using the Eagan 65mmphi T-die making machine, and the antistatic film with a thickness of 100 micrometers was fabricated.

(3) It selected in the combination which shows the manufacture above-mentioned low foaming sheet and antistatic film of a laminating sheet in a table 3, Oriental Morton ADOKOTO 305 was used as adhesives, it was stuck by pressure at 50 degrees C using the dry laminator by the equipment modern company, and the laminating sheet was made.

(4) The vacuum forming of a vacuum forming, next this laminating sheet was covered and carried out to the vacuum forming machine made from ASANO (M330 mold), and deep drawing was performed. The greatest depth which can perform good deep-drawing shaping was measured without having torn the foaming cel or a hole's opening on a laminating sheet. The result is shown in a table 3 with the antistatic nature assessment result of a laminating sheet.

[0036]

[A table 1]

表 1

		低発泡シート						
		A	B	C	D	E	F	G
配 合 組 成	樹脂 (重量) 種類							
	LDPE	100	-	-	-	100	100	100
	EVA	-	100	-	-	-	-	-
	HDPE	-	-	100	-	-	-	-
	L-LDPE	-	-	-	100	-	-	-
	物性							
	MFR (g/10分)	4	0.5	0.6	0.8	4	4	0.3
	MT (g)	5	11	9	5	5	5	12
	Q値	6.2	5.5	5.6	7.0	6.2	6.2	6.0
	発泡剤 (x100 重量)							
評 価	AA	5	5	5	5	-	-	30
	CS	-	-	-	-	7	-	-
評 価	発泡倍率 (倍)	1.5	1.5	1.5	1.5	1.7	1.0	7.0
	発泡セル寸法 (mm)	0.3	0.15	0.2	0.3	0.2	0	0.15

AA : アゾジカルボンアミド

CS : 重炭酸ソーダ・クエン酸の 1 : 1 混合系

[0037]

[A table 2]

表 2

配 合 組 成 (重量部)	帯電防止フィルム					
	a	b	c	d	e	f
樹脂						
HDPE	100	100	100	-	100	-
EPP	-	-	-	100	-	100
帯電防止剤						
グリセリン脂肪酸エステル	0.1	-	-	0.3	-	-
ポリグリセリン脂肪酸エステル	-	0.2	-	-	-	-
N,N-ビス(2-ヒドロキシエチル)脂肪酸アミン	-	-	0.1	-	-	-

[0038]

[A table 3]

表 3

		実 施 例								比較例			
		1	2	3	4	5	6	7	8	1	2	3	4
低発泡 シート	A	○	-	-	-	-	○	○	○	○	○	-	-
	B	-	○	-	-	-	-	-	-	-	-	-	-
	C	-	-	○	-	-	-	-	-	-	-	-	-
	D	-	-	-	○	-	-	-	-	-	-	-	-
	E	-	-	-	-	○	-	-	-	-	-	-	-
	F	-	-	-	-	-	-	-	-	-	-	○	-
	G	-	-	-	-	-	-	-	-	-	-	-	○
帯電防止 フィルム	a	○	○	○	○	○	-	-	-	-	-	○	○
	b	-	-	-	-	-	○	-	-	-	-	-	-
	c	-	-	-	-	-	-	○	-	-	-	-	-
	d	-	-	-	-	-	-	-	○	-	-	-	-
	e	-	-	-	-	-	-	-	-	○	-	-	-
	f	-	-	-	-	-	-	-	-	-	○	-	-
真空成形絞り 深さ (×10 mm)		13	15	13	13	15	13	13	13	13	13	-	3
帯電圧半減期 (秒)		5	5	5	5	5	*A	*A	*A	*B	*B	5	5

○：積層に使用したもの。

\*A：2秒以下    \*B：180秒以上